

THE ABSORPTION SPECTRA OF VARIOUS POTASSIUM,  
URANYL, URANOUS AND NEODYMIUM SALTS IN  
SOLUTION AND THE EFFECT OF TEMPERA-  
TURE ON THE ABSORPTION SPECTRA OF  
CERTAIN COLORED SALTS IN  
SOLUTION.

(PLATES VII. TO XIV.)

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#### I. EXPERIMENTAL METHODS.

On account of the large number of bands in the absorption spectra of uranium and the rare earth salts, a study of the absorption spectra of these salts is more interesting and more fruitful of results than the study of the absorption spectra of the ordinary colored salt like those of nickel or copper. The absorption spectra have been mapped for potassium ferricyanide, potassium ferrocyanide, potassium chromate, potassium dichromate, the acetate, bromide, chloride, nitrate and sulphate of uranyl in water, of uranyl acetate, nitrate and chloride in methyl alcohol, and of uranyl nitrate and chloride in ethyl alcohol. Beer's law has been tested for these salts as well as the effect of foreign substances on the absorption spectra. The absorption spectra of two uranous salts, the chloride and sulphate, have been photographed and the absorption spectra of neodymium chloride in pure glycerol and in mixtures of glycerol and water have been studied. In this work the methods used by Jones and Uhler<sup>1</sup> and Jones and Anderson<sup>2</sup> have in the main been employed.

The investigations on the effect of changes in temperature on the absorption spectra of solutions have been confined to different concentrations of aqueous solutions of the chloride, nitrate, acetate,

<sup>1</sup> Publication No. 60, Carnegie Institution of Washington.

<sup>2</sup> Publication No. 110, Carnegie Institution of Washington.

sulphate and sulphocyanate of cobalt, the chloride, acetate and sulphate of nickel, the chloride, sulphate and acetate of chromium, chrome alum, the nitrate and bromide of copper, uranous chloride, erbium chloride, the chloride and nitrate of præsodymium, the sulphate, acetate, chloride and nitrate of uranyl and the chloride, bromide and nitrate of neodymium. Spectrograms are made of the absorption spectra for a given concentration of a salt, keeping the thickness of layer constant for every  $15^\circ$  between  $0^\circ$  and  $90^\circ$  C.

To make a spectrogram light from a Nernst glower and from a spark is allowed to pass through the solution that is being investigated. It is then focused upon the slit of a spectroscope—and falling then on a concave grating, the light is spread out into a spectrum on the film upon which it is photographed. The films used were made by Wratten and Wainwright of Croyden, England, and were very uniformly sensitive to light from  $\lambda 2100$  to  $\lambda 7200$ .

The sectional diagram (Fig. 1) will make the experimental arrangement of the apparatus clearer. *N* is a Nernst glower which is arranged to slide along the rod *AB*. *P* and *P'* are quartz prisms which are held by a lid *L*. The prism *P* is stationary, whereas the prism *P'* can be moved by the travelling carriage *E* back and forth through the trough *T* which contains the solution whose absorption spectrum is being investigated. *AB* is so inclined that the optical length of the light beam from *N* to *P*, *P* and the concave mirror *M* shall be constant, whatever the length of the solution between *P* and *P'* may be. The greatest length of path *PP'* used was 200 mm. The hypotenuse faces of *P* and *P'* are backed by air films which are enclosed by glass plates cemented to the quartz prisms.

Considerable difficulty was experienced in finding a cement that would adhere to the polished quartz prisms at the higher temperatures. For aqueous solutions baked caoutchouc was found to work fairly well. *D* is a brass box holding the trough *T*. *D* is filled with oil and is placed in a water-bath whose temperature can be varied between  $0^\circ$  and  $90^\circ$  C. The path of a beam of light is then from the Nernst glower (*N*) or spark to the quartz prism *P'*. The light is totally reflected from the hypotenuse face of this prism through the solution to *P*. This prism also has its hypotenuse face backed by an air-film, so that the light is totally reflected upwards to the

concave speculum mirror at *M*. *M* focuses the light on the slit of the Rowland concave grating spectroscope, *G* being the grating and *C* the focal curve of the spectrum. The prism arrangement was designed by Dr. John A. Anderson.

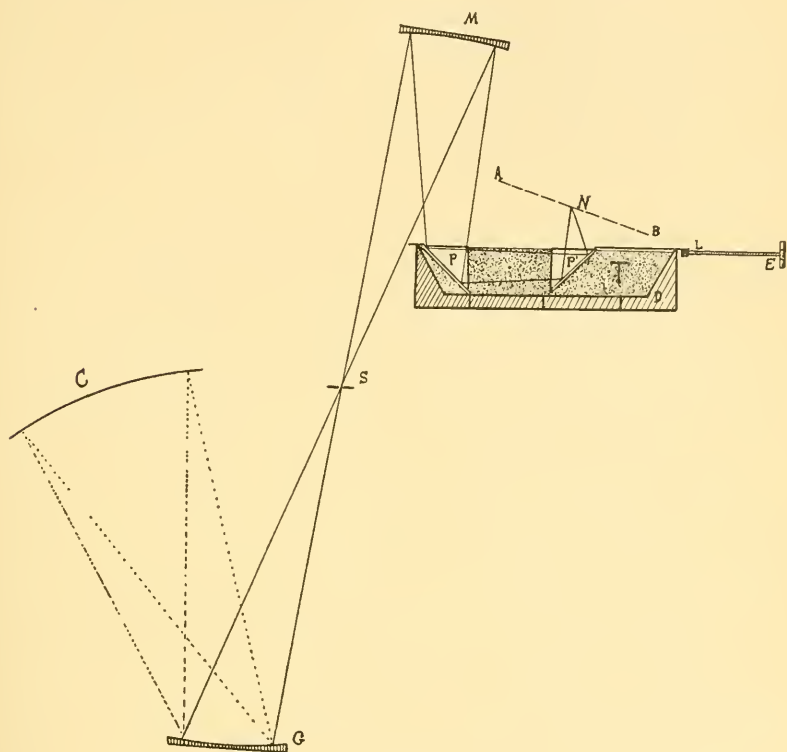


FIG. 1.

This apparatus was found to work very well for aqueous solutions. Some evaporation took place at the higher temperatures, but distilled water was added in proper quantity and mixed with the solution so as to keep the concentration constant. By using troughs of different lengths it was possible to vary the length of salt solution through which the light beam passed from 1 to 200 mm. One inconvenience was experienced at low temperatures; moisture would sometimes condense upon the exposed prism faces. To overcome this an air blast was directed upon these faces and this helped very materially to prevent the condensation of moisture.

## II. ABSORPTION SPECTRA OF POTASSIUM SALTS IN AQUEOUS SOLUTIONS.

Most potassium salts in solution are colorless, and for this reason it is considered that the potassium atoms do not themselves absorb any light in the visible portion of the spectrum. Several colored potassium salts are known and the color of these is due in some way to the other atoms in the salt molecules. In the present work the absorption spectra of potassium ferricyanide, potassium ferrocyanide, potassium chromate and potassium dichromate have been studied.

Using a 3 mm. length of solution of potassium ferricyanide in water we find that for a normal concentration there is complete absorption of all the shorter wave-lengths of light beyond  $\lambda 4800$ . As the concentration is decreased the edge of transmission moves continually towards the violet. It should be noticed that the region between complete absorption and complete transmission for the more concentrated solutions is quite narrow, being less than 40 Ångström units; thus making solutions of this salt quite good screens for absorbing light. Continually decreasing the concentration we reach a 0.0156 normal solution, when a transmission band begins to appear. For a certain range of concentration there appears an absorption band in the region  $\lambda 4200$ . Further decrease in concentration results in increasing transmission throughout the violet and ultra-violet. For dilutions greater than 0.00195 normal there is almost complete transmission throughout the ultra-violet. Very faint bands appear in the regions  $\lambda\lambda 2500$  to  $2600$ ,  $\lambda\lambda 2950$  to  $3050$  and  $\lambda\lambda 3200$  and  $3250$ .

Several spectrograms were made, keeping the product of concentration and depth of solution layer constant. In this case the spectrograms will be identical if Beer's law holds. Beer's law was found to hold according to this method of testing within the ranges of concentration over which the spectrum was mapped.

The absorption of aqueous solutions of potassium ferrocyanide was investigated in the same way. A half-normal solution 3 mm. deep shows that all light of shorter wave-length than  $\lambda 3950$  is absorbed. Keeping the depth of layer the same, it is found that

with decrease in concentration the transmission gradually moves towards the ultra-violet, and for dilutions greater than 0.0078 normal there is transmission throughout the whole spectrum. Beer's law was found to hold.

A 2-normal aqueous solution of potassium chromate 3 mm. in thickness, shows complete transmission of wave-lengths greater than  $\lambda$  4950. Decreasing the concentration causes the transmission to move gradually towards the violet and for a 0.01 normal solution a transmission band appears at  $\lambda$  3100, or, in other words, there appears an absorption band whose center is about  $\lambda$  3700. As the concentration decreases this absorption band fills up, the violet edge of the transmission band gradually pushes out into the ultra-violet, and for dilutions greater than 0.0005 normal there is complete transmission throughout the spectrum. Beer's law was found to hold for potassium chromate throughout the above ranges of concentration, except in the more concentrated solutions between 2 normal and 0.25 normal.

Potassium dichromate in water was found to have a much greater absorbing power than the solutions previously described. A one-third normal concentration absorbed all wave-lengths shorter than  $\lambda$  5350. As the concentration is decreased the transmission extends farther and farther out into the violet. For a 0.0026 normal concentration a transmission band appears in the violet, thus giving an absorption band whose center is about  $\lambda$  3800. As the concentration is further decreased transmission becomes greater and greater in the violet and ultra-violet, and is practically complete for a 0.0006 normal concentration. Beer's law has been tested between the above ranges of concentration and has been found to hold.

In photometric measurements of Beer's law, the equation defining the quantities to be measured is:

$$J = J_0 10^{-Acl}$$

$J_0$  is the intensity of the light that enters the solution (neglecting any loss due to reflection),  $J$  the intensity of the light as it leaves the solution,  $c$  the concentration in gram molecules of the salt per liter of solution,  $l$  the thickness of layer and  $A$  a constant if Beer's law holds. Strictly speaking the above equation holds for mono-

chromatic light. For ordinary white light one would have to integrate this equation over the range of wave-lengths used. The equation would then have the form

$$J = J_0 \int_{\lambda_1}^{\lambda_2} e^{-\beta l c} d\lambda.$$

The quantity  $\beta$  is called the index of absorption and  $A$  the molecular extinction coefficient. If the absorption is proportionately greater in the more concentrated solutions, then Beer's law fails and  $A$  decreases inversely as the concentration.

From photometric measurements Settegast<sup>3</sup> and Sabatiér<sup>4</sup> conclude that the absorption spectrum of potassium dichromate is the same as that of chromic acid, and that the absorption spectrum of potassium chromate is entirely different. This is corroborated by the present work. Settegast finds that Beer's law does not hold for potassium chromate and potassium dichromate, the coefficient  $A$  decreasing with increasing concentration. Grünbaum<sup>5</sup> finds the following values of  $A$  and  $\epsilon$  where  $\epsilon = c/A$ .

<i>Potassium Dichromate.</i>		
$\lambda$	Value of $A$ .	Value of $A$ .
	$c = .034$	$c = .0034$
509	62.4	58.0
521	28.7	26.2
538	7.24	6.2

It will be seen that the deviation here from Beer's law is in the opposite direction from that of Settegast. Grünbaum finds that  $\epsilon$  and therefore  $A$  depends on the depth of layer.

An example will be given where the same concentration was used and different depths of the solution.

$\lambda$	Values of $\epsilon$ for $c = .0034$		
	25 cm. layer.	12 cm. layer.	5 cm. layer.
521	.0758	.0818	.0884
521	.0761	.0830	.0897

Our work indicates that Beer's law holds for all small concentrations and usually the deviations for concentrated solutions is very

<sup>3</sup> *Wied. Ann.*, 7, pp. 242-271, 1879.

<sup>4</sup> *C. R.*, 103, pp. 49-52, 1886.

<sup>5</sup> *Ann. d. Phys.*, 12, pp. 1004, 1011, 1903.

small. Of the potassium salts above described, only potassium chromate between 2 normal and 0.25 normal showed any considerable deviation from Beer's law, and in this case the absorption of the concentrated solution was greater than would be expected if Beer's law held by about 40 Ångström units.

The present method is a very good qualitative test of Beer's law, and gives the results for each wave-length, whereas most photometric methods only give integrated results over a more or less wide region of wave-lengths.

### III. ABSORPTION SPECTRUM OF URANYL NITRATE UNDER DIFFERENT CONDITIONS.

There are two groups of uranium salts, the uranyl salts containing the  $\text{UO}_2$  group, and the uranous salts. The uranyl salts in solution are yellow and usually crystallize from aqueous solutions with a certain amount of water of crystallization; for example, at ordinary temperatures uranyl sulphate crystals have the composition  $\text{UO}_2(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$ . The uranous salts are intensely green and are very unstable, oxidizing very easily to the uranyl condition. Uranous sulphate crystals have the composition  $\text{U}(\text{SO}_4)_2 \cdot 9\text{H}_2\text{O}$ .

#### (a) *Uranyl Nitrate in Aqueous Solution.*

The spectrum of uranyl nitrate in water is a typical example of the uranyl salts. Using a depth of solution of 3 mm. its absorption spectra was investigated between concentrations of 1.5 normal to 0.0234 normal. For the 1.5 normal solution the absorption consists of a band in the blue-violet and absorption throughout the ultra-violet portion of the spectrum. As the concentration decreases the blue-violet band fills up with transmission, and the ultra-violet absorption is pushed farther and farther out into the ultra-violet. The blue-violet band is practically gone at a concentration of 0.5 normal, and there is almost complete transmission throughout the ultra-violet for concentrations less than 0.02 normal.

During these changes in concentration a large number of bands about 50 Ångström units wide make their appearance. Near the edge of an absorption band these bands are relatively quite clear.



As the absorption edge recedes from the uranyl bands, the general transmission is so great as almost to entirely obscure them.

*A*, Plate I, represents the absorption spectra of an aqueous solution of uranyl nitrate of different depths of layer. The narrow and rather weak bands shown here are the uranyl bands. Twelve of these bands have been photographed. Starting at the band of longest wave-length they shall be designated by the letters *a*, *b*, *c*, *d*, etc. On account of the irregularity of the distribution of light in the spark spectrum and the small intensity of the uranyl bands, the Nernst glower was used as the source of light in the ultra-violet, and long exposures were made. A screen was used that cut out all wave-lengths greater than  $\lambda 4200$ . *A* represents a typical spectrogram of this kind. Starting with the spectrum strip at the top, the concentrations were 1.5 N, 1.125 N, 0.75 N, 0.5 N, 0.375 N, 0.25 N, and 0.1875 N. The slit width was 0.08 mm. and the current through the Nernst glower 0.8 amperes. The spectra of wave-lengths greater than  $\lambda 4300$  represent the absorption of a depth of layer of 15 mm.; the spectra of shorter wave-lengths represent the absorption of a depth of layer of 3 mm. The upper spectrum strip represents then the absorption spectrum of a 1.5 normal solution of uranyl chloride 15 mm. thick, exposure being made 1 min. to the Nernst glower. It will be seen that the uranyl *a* band comes out very strongly. The screen was then placed in the path of light and exposure of 5 minutes made to the violet and ultra-violet beyond  $\lambda 4300$ ; a solution of uranyl nitrate of 1.5 normal concentration and 3 mm. depth of cell being in the path of the beam of light. This amount of uranyl nitrate absorbed practically all the light in this region. A very short exposure was afterwards made to the spark in the region  $\lambda 2600$ , in order to get a comparison spark spectrum in this region, so that the wave-lengths of the uranyl bands could be measured.

Throughout this work a comparison spark spectrum usually containing the very strong line  $\lambda 2478.8$  was photographed on each spectrum strip. In measuring the uranyl bands all measurements were made from this line as a standard, and although the absolute wave-lengths of the uranyl bands may not be correct to within 20

Ångström units, yet their relative accuracy is probably correct to within less than 10 Ångström units for the finer bands.

The second spectrum strip from the top represents in the long wave-length end of the spectrum the absorption of a 15 mm. solution of a 1.125 normal solution of uranyl nitrate exposed 1 min. to the Nernst glower. The *a* band appears, although not nearly as intense as in the spectrum strip above. The region of shorter wave-lengths beyond  $\lambda 4300$  represents the absorption of a 3 mm. depth of layer of a 1.125 normal concentration exposed 5 min. to the Nernst glower. A very faint transmission is shown in the region  $\lambda 3700$ . The ultra-violet line  $\lambda 2478.8$  is shown in the comparison spark spectra. The other spectrum strips were made in a similar manner, using the concentrations given above.

By this method of exposing two new bands were detected in the ultra-violet. In aqueous solutions the intensities of the bands are much the same. In other solvents however and for other uranyl salts, the relative intensities of the bands change very greatly. In uranyl nitrate crystals the bands are even more closely related to each other than in aqueous solutions. The longer the wave-length of the band the more intense and wider it is as a rule. The position of the long wave-length bands in the orthorhombic uranyl nitrate crystals  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  is the same as the position of the bands for an aqueous solution. The wave-lengths of the bands are as follows:

	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>	<i>g</i>	
Water Sol.	4860	4720	4540	4380	4290	4150	4020	Deussen.
Water Sol.	4870	4705	4550	4390		4155	4030	} Jones and Strong.
Crystals	4870	4705	4500-4565	4405	4275	4170	4050	
		<i>h</i>	<i>i</i>	<i>j</i>	<i>k</i>	<i>l</i>		
Water Sol.		3870	3790	3690				Deussen.
Water Sol.		3905	3815	3710	3605	3515		} Jones and Strong.
Crystals		3935	3830	(3720?)	3600			

In the original film from which *A*, Plate I, was made all these bands except *d* could be very distinctly seen. The bands of longer

wave-length are slightly wider. The *i* band is considerably weaker than its neighboring bands.

(b) *Absorption Spectrum of Uranyl Nitrate Crystals.*

In the aqueous solution there is no sign that the bands can be broken up. In the crystal spectrum this is not the case. The *a* band is narrow. The *b* band is also very narrow, about 15 Ångström units wide. A very faint band appears about  $\lambda 4650$ . The *c* band, on the other hand, is very wide, about 70 Ångström units, and is probably double. The *d* band is about 50 Å. u. wide, and the *e* band is about 70 Ångström units wide and appears double. The *f* band is the most intense and is about 40 Å. u. wide. The bands *g*, *h*, *i* and *j* keep decreasing in intensity respectively. The above description is of a spectrogram taken of a crystal in Canada balsam, and of course the width of the bands varies with the time of exposure and various other things. The above spectrogram showed many details, however, that other spectrograms did not. It will thus be seen that the *a*, *b*, *c*, *d*, *j* and *k* bands of the solution agree fairly well with those of the crystal, and that the crystal bands *f*, *g*, *h* and *i* are shifted towards the red with reference to the bands in the aqueous solution.

(c) *Effect of Dilution upon the Uranyl Bands.*

The effect of dilution on the position and intensity of the blue-violet, the ultra-violet and the uranyl bands of the acetate, nitrate and sulphate of uranyl in water was tried. The absorption spectra of solutions of about 1 normal and 3 mm. depth of cell was photographed along by the side of the absorption spectra of the same salts of 0.008 normal concentration and 380 mm. depth of layer. The absorption consisted of the blue-violet band, the ultra-violet band and the *a*, *b*, *c*, *i*, *j* and *k* bands. Between the blue-violet and ultra-violet bands there was the transmission band containing *i*, *j* and *k*. For each of the three salts this transmission band was much weaker for the dilute solution, whereas in the cases of the sulphate and nitrate the long wave-length transmission edge of the blue-violet band was stronger for the more dilute solution. The opposite was true of the acetate solution. In the dilute solution of

the acetate the bands were more intense than for the more concentrated solution. There was no noticeable change in the position of the bands. Neither the intensity nor the position of the uranyl nitrate or the uranyl sulphate bands was changed by the above dilution.

A more detailed study was made as to whether Beer's law holds for uranyl nitrate and for the other uranyl salts. The method of taking the spectrograms is the same as that used for the potassium salts.

Beer's law was found to hold for dilute solutions of uranyl nitrate in water. When the concentration is greater than .5 normal the absorption is greater than it should be if Beer's law held.

(d) *Uranyl Nitrate in Methyl Alcohol.*

In methyl alcohol the general appearance of the absorption is very similar to that of the aqueous solution; the blue-violet, the ultra-violet, and uranyl bands appearing under the same general conditions that they appear for aqueous solutions. There is a very marked deviation from Beer's law for the more concentrated solutions, however; the absorption of concentrated solutions being greater than it would be if Beer's law held. The positions of the bands are quite different from the positions of the uranyl bands of the aqueous solution, or of the crystals, as shown by the following values:

	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>	<i>g</i>	<i>h</i>	<i>i</i>
$\lambda$	4930	4760	4610	4455	4325	4190	4070	3965	3855

(e) *Uranyl Nitrate in Mixtures of Methyl Alcohol and Water.*

In the previous work of Jones and Anderson<sup>6</sup> it was found that in some cases (for example neodymium chloride) a salt in water had a different set of absorption bands compared with the same salt in another solvent as, *e. g.*, methyl alcohol.

When the salt is dissolved in mixtures of these two solvents, say methyl alcohol and water, it was found that as the amount of one solvent, methyl alcohol for instance, decreased the methyl

<sup>6</sup> Publication No. 110, Carnegie Institution of Washington.

alcohol bands of the salt decreased in intensity, but did not change their position in the spectrum. At the same time the water bands of the salt became more intense. In the present work it is shown that the uranyl nitrate bands in pure water and in pure methyl alcohol occupy different positions. The problem to be investigated is to find out whether in mixtures of water and methyl alcohol, the uranyl bands will show a gradual shift, or whether the methyl alcohol uranyl bands and the water bands will both exist together; their relative intensities being proportional to the relative amounts of methyl alcohol and water. It was found that the two sets of bands exist together and that the methyl alcohol bands decrease in intensity quite rapidly with increase of water. The blue-violet band showed marked changes until the amount of water reached about 20 per cent. In this work the amount of uranyl nitrate in the path of the light was kept constant, and the only variable was the relative amounts of methyl alcohol and water. The above would indicate that uranyl nitrate in water is "hydrated" and in methyl alcohol it is "alcoholated." The above data indicate that the effect of "hydration" is much more persistent than that of "alcoholation." It is quite possible that this is due to a greater number of water molecules producing the hydration than there is methyl alcohol molecules taking part in alcoholation.

(f) *Uranyl Nitrate in Ethyl Alcohol.*

The absorption of uranyl nitrate in ethyl alcohol was mapped and the general characteristics were found to be the same as for the water and methyl alcohol solutions. A new band was found at  $\lambda$  5200 which was about 50 Ångström units wide. All the uranyl bands were very faint and wide and therefore difficult to measure. Beer's law showed deviations similar to those found for the methyl alcohol solution. On account of the diffuseness of the bands no spectrograms were made of mixtures of water and ethyl alcohol. Following are approximately the positions of a few of the bands:

	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>	<i>g</i>	<i>h</i>	<i>i</i>
$\lambda$	5000	4800	4630	4475	4325	4180	4080	3970	3875

(g) *Absorption Spectrum of Anhydrous Uranyl Nitrate.*

When it was first discovered that the uranyl nitrate "water" bands were all shifted to the violet with reference to the bands of the other uranyl salts in water, as well as with reference to the uranyl nitrate bands in other solvents, it was thought that possibly it was more hydrated than the other salts in solution. The uranyl salts crystallize from water solutions at ordinary temperatures with the following composition:  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{UO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ ,  $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ , and  $\text{UO}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ . This fact would favor the supposition that in solution the nitrate might be more hydrated than the other salts. The fact that the absorption of the aqueous solution of the nitrate and the crystallized salt was very much the same as far as the positions of the uranyl bands is concerned, also seemed to favor this view.

In this connection it was considered important to examine the absorption spectrum of the anhydrous uranyl nitrate. The salt was powdered and placed in a closed glass tube just above the slit of the spectroscope. The light of a Nernst glower was then focused upon the surface of the salt nearest the slit and an exposure of about three hours made. In this way we examine light that has penetrated a short distance into the powder and is then diffusely reflected.

The absorption spectrum was found to consist of quite a large number of bands, which seem quite different in many respects from those of the solution. The following are the approximate wavelengths:  $\lambda\lambda$  4800, 4650, 4500, 4420, 4360, 4280, 4180 (broad), 4060 (broad), 3950 (broad), 3820 (broad), 3700 (narrow) and 3600 (narrow). The bands marked broad are from 50 to 60 Ångström units wide and the narrow bands about 20 Ångström units. If the first band is the *a* band, then the bands of the anhydrous salts are to the violet of the corresponding bands of the crystals and of the solution. If it is the *b* band the opposite is the case. On account of the smallness of the intensity of the bands it could not be settled whether  $\lambda$  4800 is the *a* or the *b* band. Further investigation of this point will be made.

There are two difficulties to the above theory, difficulties for

which no explanation so far has been suggested. In the work on the effect of rise of temperature on the absorption spectrum it was found that the uranyl nitrate bands did not shift to the red. On the other hand, the uranyl sulphate and uranyl chloride bands were shifted to the red under the same conditions. (In these cases aqueous solutions were investigated.) If the uranyl nitrate bands owe their position to a large amount of hydration it would be expected that with rise in temperature they would be shifted towards the red more than the bands of the sulphate and chloride. Another difficulty is that of the effect of dilution. The greater the dilution the greater the dissociation, and, therefore, according to the theory of Arrhenius for very dilute solutions the  $\text{UO}_2$  group should exist in the ionic condition and the absorption spectrum of all the salts should be the same, *i. e.*, the uranyl bands should then occupy the same positions independent of the kind of salt. No effect of this kind is to be noticed, as was shown above under the division describing the effect of dilution. It is intended to use much more dilute solutions in the future.

#### IV. THE ABSORPTION OF URANYL BROMIDE, URANYL ACETATE AND URANYL SULPHATE.

##### (a) *Absorption Spectrum of Uranyl Bromide in Water.*

The absorption spectrum of uranyl bromide in water was mapped and found to be very similar to that of the nitrate. The ultra-violet, blue-violet and uranyl bands appear and are affected in the same manner as the same bands of the nitrate. Beer's law was found to hold. The uranyl bands were found to be much wider and more diffuse than in the case of the aqueous solution of the nitrate. The following are their approximate positions:

<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>
4880	4720	4560	4450	4280	4160

##### (b) *Uranyl Acetate in Water, Beer's Law.*

A spectrogram was made to test whether Beer's law holds for an aqueous solution of uranyl acetate between the concentrations 0.25 normal and 0.031 normal. The spectrogram showed that there was a very great deviation from the law, and in the opposite direc-

tion to any deviation hitherto found either in this work or in that of Jones and Anderson or Jones and Uhler. The absorption of the more dilute solutions was found to be proportionately much greater than for the more concentrated solutions. A similar run was made for a solution of the acetate in methyl alcohol and a deviation from Beer's law in the same direction was found, although the amount was not so great in this case.

(c) *The Uranyl Bands of the Acetate.*

The following table gives the approximate wave-lengths of the uranyl bands of the acetate in water, in methyl and as the anhydrous powder.

*Bands of Uranyl Acetate.*

	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>	<i>g</i>	<i>h</i>	<i>i</i>
In Water	4910	4740	4595	4455	4310	4160	4070	3970	3830
In Methyl Alcohol	4900	4770	4600	4460	4320	4200	4090		
As Anhydrous Salt.	4910	4760	4610	4460	4330	4190	4070	3980	

From this table it seems that the positions of the bands of the acetate under these different conditions is about the same.

(d) *Absorption Spectrum of Uranyl Sulphate.*

The mapping of the absorption spectrum of uranyl sulphate in water showed that it was very much like that of the nitrate in water. As in the case of the nitrate the *i* band was much weaker than the adjacent bands. Beer's law was found to hold. The addition of a large amount of sulphuric acid was found to make the uranyl bands much sharper, but not to cause them to shift. Much more work will be done on the effect of strong acids on the uranyl bands. The following gives the wave-lengths of the sulphate bands:

<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>	<i>g</i>	<i>h</i>	<i>i</i>	<i>j</i>	<i>k</i>	<i>l</i>
4900	4740	4580	4460	4330	4200	4070	3970	3850	3740	3630	3530

V. THE ABSORPTION OF NEODYMIUM CHLORIDE IN GLYCEROL AND MIXTURES OF GLYCEROL AND WATER.

The absorption spectrum of a glycerol solution of neodymium chloride is much like that of the aqueous solution in its general



characteristics, but when proper concentrations are used so as to bring out the fine bands it is found that the two spectra are entirely different. For example, the aqueous solution shows a very fine band at  $\lambda 4274$ . In the glycerol there is a band that on first sight appears exactly identical with this 4274 band. However, its wavelength is about  $\lambda 4287$ , and it has two extremely fine components on each side, one at  $\lambda 4273$  and one at about  $\lambda 4300$ . The same is true throughout the spectrum.

In general, in mixtures of water and glycerol the appearances indicate that there are "glycerol" bands and "water" bands and as the amount of one solvent is increased, so are the bands corresponding to this solvent increased in intensity. Herein lies a very large field for investigation and considerably more work is being carried on here along these lines. The above described spectrum of the glycerol solution of neodymium indicates that glycerol has a very great influence upon the vibrations of the electrons within the neodymium atom—and that this is due to a kind of "atmosphere" of glycerol about the neodymium atom. Jones and Anderson showed that alcohol has a similar effect, and that the "alcohol" bands were much less persistent than the water bands. Further work is being done upon the relative persistence of "water," "alcohol" and "glycerol" bands; also on the effects of foreign substances and rise of temperature upon these bands, both in the pure solvent and for mixtures of solvents.

## VI. ABSORPTION SPECTRUM OF URANYL CHLORIDE.

The absorption spectrum of uranyl chloride was mapped for an aqueous solution, a methyl alcohol solution, an ethyl alcohol solution, a mixture of methyl alcohol and water, a mixture of methyl alcohol and calcium chloride, and a mixture of water and aluminium chloride.

### (a) *The Absorption Spectrum of Uranyl Chloride in Water.*

The absorption spectrum of uranyl chloride in water was found to be very similar in general to that of the other uranyl salts. The uranyl bands were less sharp than the bands of the nitrate and sulphate in water. The wave-lengths of a few of the bands are as follows:

<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>	<i>g</i>
4920	4740	4560	4460	4315	4170	4025

(*b*) *Absorption Spectrum of Anhydrous Uranyl Chloride.*

The absorption spectrum of the anhydrous uranyl chloride was photographed in the same way as that of the anhydrous nitrate. The bands differ considerably from the bands of the aqueous solution, and one cannot tell very well whether they are identical with the corresponding *a*, *b*, *c*, etc., bands of the solution or not. Their wave-lengths are approximately as follows:  $\lambda\lambda$  4950 (narrow), 4860, 4765, 4700, 4615, 4540, 4460, 4320, 4290, 4160, 4050 and 3940.

(*c*) *The Characteristic Bands of Uranyl Chloride.*

In addition to the bands already described, uranyl chloride has several remarkably fine bands in the green. These bands are not more than 5 Ångström units wide and were first seen on spectrograms taken upon Whatten and Wainwright red sensitive films. They appear only for aqueous solutions, and the addition of calcium chloride or aluminium chloride causes them to disappear. They do not appear in alcoholic solutions. Aqueous solutions of uranyl sulphate show them very faintly. The wave-lengths are approximately as follows:

$\lambda\lambda$  5185, 5200, 6000, 6020, 6040 and 6070.

These bands have never hitherto been noticed as absorption bands. H. Becquerel<sup>†</sup> gives quite a full set of measurements of the phosphorescent bands of various uranyl salts at room temperature and at the temperature of liquid air. Among the bands given for the double chloride of uranyl and potassium at room temperature are  $\lambda\lambda$  6070 to 6040, and  $\lambda\lambda$  5220 to 5193. Whether these correspond to the above absorption bands is quite difficult to say. Further work is being done in this direction.

(*d*) *Uranyl, Calcium and Aluminium Chlorides in Water.*

Spectrograms were taken of aqueous solutions of a constant concentration of uranyl chloride to which varying amounts of calcium

<sup>†</sup> C. R., t. 101, p. 1252, 1885; pp. 459 and 621, 1907.

chloride were added. The addition of calcium chloride causes the ultra-violet, the blue-violet band and the uranyl bands to widen generally. The effect upon the uranyl bands is however, very small. The effect of aluminium chloride, however, is very great. The two narrow and faint bands at  $\lambda 5200$  only appear in the pure aqueous solution of uranyl chloride. The *a* band in the aqueous solution is about 60 Ångström units wide, and is almost as intense as the *b* band. The addition of aluminium chloride causes the band to become quite narrow, about 25 Ångström units wide. A slight addition of aluminium chloride decreases the intensity of the band very considerably. Further increases in the amount of aluminium has very little effect. The addition of aluminium also causes the bands to shift to the red; the shifts in some instances amounting to 25 Ångström units. The *b* and *c* bands have their intensity very greatly increased by the addition of aluminium chloride; and by making the solution about 2 normal of aluminium chloride these bands are shifted about 30 Ångström units to the red compared with the same bands for the pure uranyl chloride solution. The *d*, *e*, *f*, *g* and *h* bands are also increased in intensity, but are but very slightly shifted to the red. The *d* and *e* bands are widened so that they practically form a single band.

(e) *Absorption Spectrum of Uranyl Chloride in Methyl Alcohol.*

In the absorption spectrum of uranyl chloride in methyl alcohol the *a*, *b*, *c*, *d*, *e*, *f*, *g*, *h*, *i*, and *j* bands all appear, the *b* and *c* bands being the largest and most intense. The following are the approximate wave-lengths of the bands:

	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>	<i>g</i>	<i>h</i>	<i>i</i>	<i>j</i>
Uranyl Chloride in										
Methyl Alcohol	4930	4760	4590	4465	4345	4220	4090	3980	3860	3760
Uranyl Nitrate in										
Methyl Alcohol	4930	4760	4610	4460	4325	4190	4070	3970	3855	
Uranyl Acetate in										
Methyl Alcohol	4900	4770	4600	4460	4320	4200	4090			

It is seen from the above table that the uranyl bands of these three salts in alcohol occupy almost exactly the same positions.

(f) *Absorption Spectrum of Uranyl Chloride and Calcium Chloride in Methyl Alcohol.*

In the solution of uranyl chloride in methyl alcohol the *d* and *e* bands are very diffuse, but are entirely separate. By adding calcium chloride a very peculiar phenomenon takes place. The *d* and *e* bands come together and as far as one can tell form a single band. At the same time the *f*, *g* and *h* bands shift to the red. For a solution containing a .9 normal solution of calcium chloride one finds that the *b* and *c* bands have practically remained in the same position, the *d* and *e* bands have merged into one and the *f*, *g*, *h* bands have moved to approximately  $\lambda\lambda 4260$ ,  $4120$  and  $4010$  respectively. The *de* band is approximately at  $\lambda 4420$ .

(g) *Absorption Spectrum of Uranyl Chloride in Methyl Alcohol and Water.*

A spectrogram was made of a solution of uranyl chloride of constant concentration in mixtures of methyl alcohol and water. A small addition of water causes a considerable decrease in the absorption power of the uranyl chloride. When the amount of water has reached about 16 per cent. very little further change is produced by further increasing the amount of water. The most important effect of the addition of water is the effect upon the uranyl bands. For a pure alcoholic solution the *a* and *b* bands appear; the *b* band being quite intense. Adding water causes *a* and *b* to both decrease in intensity and apparently to shift towards the violet. A spectrogram of smaller concentration shows the *a*, *b*, *c*, *f*, *g*, *h* and *i* bands; the solution containing 8 per cent. water the *b*, *c*, *d*, *e*, *f*, *g*, *h*, *i* and *j* bands; the 16 per cent. water solution *b*, *c*, *d*, *e*, *f*, *g*, *h*, *i* and *j*; the 24 per cent. aqueous solution shows all these bands greatly weakened, and in solutions containing a greater amount of water practically only the *b* and *c* bands appear, and these are very diffuse. The general effect upon the positions of the bands is quite remarkable, the *b* and *c* bands apparently being shifted to the violet with increase of water, whereas the ultra-violet bands appear to be shifted towards the red.

*(h) Absorption of Uranyl Chloride in Ethyl Alcohol.*

The absorption spectrum of uranyl chloride in the ethyl alcohol shows the uranyl bands quite strongly, although they are less intense than for the methyl alcohol solution. A very interesting resemblance has been found for the various uranyl bands of different mixtures. The absorption spectrum of a solution of uranyl chloride in ethyl alcohol has been found to be almost the same as that of a methyl alcohol solution of uranyl chloride containing a 0.9 normal concentration of calcium chloride or an aqueous solution of uranyl chloride and a 2 normal concentration of aluminium chloride.

The positions of the uranyl bands for the ethyl alcohol solution was approximately:

	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>	<i>g</i>	<i>h</i>	<i>i</i>
$\lambda$	4900	4750	4580	4400	4400	4250	4100	3980	3860

The relation above mentioned comes out much better in comparing the spectrograms. The values of wave-lengths thus far given does not bring this out very well on account of the difficulty of making measurements. Much more work is to be carried on along this line, and the measurements above given are to be considered as more or less of a preliminary character.

*(i) The Blue-Violet Band.*

Under the various changes above noted, *i. e.*, of changing the acid radicle, of changing the solvent and of adding foreign substances, the position at which the blue-violet band faded away was approximately  $\lambda$  4200. This is rather unexpected when we consider the very considerable effects which are produced upon the finer bands.

## VII. ABSORPTION SPECTRUM OF URANOUS SALTS IN SOLUTION.

It is quite well known that by reduction the yellow uranyl salts are changed to the intensely green uranous salts. In the present work this reduction was accomplished by adding the same acid to the solution that corresponded to the anion of the salt and then putting in a metal that would produce a colorless salt.

The absorption spectrum of uranous sulphate and uranous

chloride in water was found to be very similar. The absorption of the shorter wave-lengths was complete under the conditions used. The following are the approximate positions of some of the bands:  $\lambda\lambda$  6700, 6500, 6300, 5480 and 4900. The 6500 band was the strongest one of all, and upon increasing the depth of cell this band widened out so as to unite with the bands  $\lambda\lambda$  6700 and 6300, forming an absorption band covering hundreds of Ångström units. This is a very characteristic property of many of the uranous bands, that of widening out so as to include a very large portion of the spectrum. The uranyl bands do not change in width very greatly on increasing the depth of cell.

Besides the bands described above uranous chloride shows bands at  $\lambda\lambda$  4600, 4770 and 4970.

The absorption spectrum of uranous chloride in methyl alcohol was found to differ very much from that of the aqueous solution. The bands at  $\lambda\lambda$  4600 and 4780 appeared, closely resembling the water bands at the same position. The band  $\lambda$  4970 in water was broken up into two bands in methyl alcohol at  $\lambda\lambda$  4930 and 5030. In the alcohol a very broad band appeared at  $\lambda$  5300, which does not appear at all in the water solution. The band at  $\lambda$  5580 is very similar to the water band. Weak and broad bands appear at  $\lambda\lambda$  6150, 6300 and 6480, and a strong band at  $\lambda$  6750. As the depth of the alcoholic solution is increased the widening of the bands is very different from the widening of the bands of the aqueous solution.

The absorption spectrum of a mixture of calcium chloride and uranyl chloride in water was found to be very similar to that of the pure uranyl water solution. Much further work along the above lines is being carried on.

#### VIII. AN EXAMPLE OF THE COMPLEXITY OF THE PROBLEM OF EXPLAINING THE ORIGIN OF SPECTRAL LINES AND BANDS AND THE PROPOSED METHOD OF ATTACK.

It is a fact that investigations upon the spectral emission and absorption of bodies has been far less fruitful in extending our knowledge of the structure of the atom than had been expected.

This is largely owing to the almost infinite complexity of the structure of the atom and our general ignorance of the forces that exist there. Probably the best known example is that of the uranyl group which we have been describing. Let us consider the spectral vibrations that can be produced by components that exist or may be produced from the apparently simple  $\text{UO}_2$  group: (1) We have the absorption spectrum described above. At low temperatures most of these bands break up into much finer bands. (2) The uranyl salts under various methods of excitation emit a phosphorescent spectrum of a large number of rather fine bands throughout the visible region of the spectrum. It is quite possible that this spectrum is intimately connected with that of the absorption spectrum. (3) We have the absorption spectrum of the uranous salts which has been described above. This spectrum has been probably caused by the change of valency of the uranium atom. Uranium is known to form quite a large number of oxides and it is quite possible that for each valency of the uranium we have a characteristic spectrum. (This also is being investigated.) It is also quite probable that at low temperatures those spectra would consist of quite fine bands. (4) We have the spark spectrum and the absorption spectrum of oxygen, and (5) that of ozone, which bears no relation to that of oxygen. (6) There is the exceedingly complex spark spectrum of uranium consisting of thousands of fine lines and also (7) the complex arc spectra. From radioactive experiments it is known that uranium is continually breaking down into ionium. (8) Ionium possesses the properties of a chemical atom and most likely has a spectrum of its own. This would make eight spectra. (9) Ionium breaks down into the radium and radium has a very characteristic spark spectrum, as does also (10) the radium emanation. During the various radioactive transformations several  $\alpha$  products are emitted with a velocity almost as great as that of light. It is probable that these particles are moving with very great velocities in the uranium atom under ordinary conditions. (11) The  $\alpha$  particles are known to be charged helium atoms and therefore under proper excitation would give the helium spectrum. The radium emanation breaks down into Radium A, B, C, D, E and F. These products behave like chemical elements

and probably have characteristic spectra. (12) The final product is lead, which has a very complex spark and arc spectra. During these transformations several electrons have been thrown off from the various products with enormous velocities. In a very large number of the above spectrum lines the Zeeman effect indicates the presence of negative electrons and charged doublets.

We thus see what an extremely complex system  $\text{UO}_2$  must be and it might seem almost hopeless to entangle the mystery of its various spectra. At present we know that the arc and spark spectra problem is very complex and that we have very few methods of producing any changes in it. Practically the only method of changing the frequency of these vibrations is by applying a very powerful magnetic field or great pressure and these changes in the frequency are very small. One very important result, however, has been accomplished by Kayser, Runge, Wood and others. This work consists in separating spectrum lines into various series. A series of lines are those whose intensity and Zeeman effect vary in the same way when the conditions outside the atom are changed. The work of Wood is very important and shows that spectrum lines are due to different systems of vibrators inside the atom. By using monochromatic light of different wave-lengths he has been able to excite different series of lines which constitute altogether the fluorescent spectrum of the element.

Present theories of the atom usually regard the electrons and other vibrators that are the sources of arc and spark lines as being far within the atom and as affected by external physical conditions only under very special circumstances. Stark believes that these electrons may rotate in circular orbits, the locus of the centers of these orbits being a closed curve, say a circle. This system will be equivalent to a positive or negative charge according to the sense of rotation of these electrons. These electrons we will call ring electrons. Supposing these systems to be positive charges, it will require electrons to neutralize these charges. Several of these neutralizing electrons may be in the outer parts of the atom and under certain conditions might be knocked off from the atom. These easily removable electrons will be called "valency" electrons, and can exist under different conditions of "looseness" of con-



nection with the atom. Most of the neutralizing electrons will probably lie far within the atom. For instance, we would expect that in the uranium atom the charged helium atoms are neutralized by negative electrons.

Our theory is that the finer absorption bands of such salts as neodymium, erbium and uranium are due to vibrations of these neutralizing electrons, and that the forces acting upon these are considerably different from those acting on the ring electrons, which, in many cases, give a normal Zeeman effect. It is probable that these neutralizing electrons play the greatest rôle in the optical properties of bodies, such as the properties determining the index of refraction, the extinction coefficient, etc.

Usually the equation of motion of such an electron is given by an equation like the following when a light wave of an electric field  $E \cos pt$  is passing by it:

$$m \frac{d^2x}{dt^2} + k \frac{dx}{dt} + n^2x = E \cos pt.$$

where  $m$  is the total mass (electromagnetic and material) of the electron,  $k \cdot dx/dt$  is the damping or frictional term and  $n^2x$  is the quasielastic force. It is an experimental fact as shown by the above work and the work of other investigators, that  $\kappa$  and  $n^2$  are not only functions of the electron and the atom, but that they are also functions of the physical and chemical conditions existing in the neighborhood of the atom.

On the other hand, the effect on  $\kappa$  and  $n^2$  for a ring electron, when external physical and chemical conditions are changed, is very small. It is for this reason, and the probable fact that there are relatively few neutralizing electrons, that we believe that much greater progress can be made in determining some of the properties and constitution of various interatomic systems of atoms and molecules by the study of the absorption spectra of uranium and neodymium than by a study of the arc or spark spectra of the same.

The method of attacking the above problem will be to study the effect on the spectra of a body produced by changing the physical and chemical conditions about the light absorbers or emitters within as wide ranges as possible. Some of the possible changes that

can be made are as follows: Take for instance the uranyl group  $UO_2$ . We can find the effect upon the absorption bands produced (1) by diluting the solution, (2) by changing the acid radicle to which the uranyl group is united, (3) by changing the solvent and using mixtures of solvents, (4) by adding other salts (like aluminium chloride), or (5) by adding acids of the same kind, as that of the salt of the uranyl group. The effect of adding foreign salts and acids at the same time and then varying the solvent, or the temperature, can also be tried. In this way a very large number of very interesting things can be tested. In most of these changes  $lc$  will be kept constant.

In the above examples the temperature (7), the external pressure (8), the electric field (9) and the magnetic field (10) can be changed between wide limits. The latter effect is a very important one. For example, in aqueous solution neodymium salts give a large number of fine bands, in glycerol there are quite a number of new bands replacing the "water" bands, and in the alcohols there are various "alcohol" bands. At low temperatures these bands become very fine and it is quite possible to detect the Zeeman effect. Now it seems quite probable that a "glycerol" band and an "alcohol" band that seem to replace each other as the solvent is changed are both due to the same vibrator. If the Zeeman effect is the same in both cases it would be a strong argument in favor of the above theory. A case that will soon be described is very important. It was found that certain neodymium lines in a pure water solution did not have their wave-length changed when the temperature was changed from  $0^\circ$  to  $90^\circ$ . If, however, calcium chloride was added, then on raising the temperature the above bands were shifted to the red. A very interesting and important investigation is whether the Zeeman effect on this band would be affected by the presence of bodies like calcium chloride.

To be compared with the above changes are changes in the absorption spectra of the crystals of the salt (11) as affected by water of crystallization, or by the presence of foreign substances, or as affected by the polarization (12) or direction of passage of light through the crystal. The absorption spectra (13) of the anhydrous powder at different temperatures, etc., should be found. The

phosphorescent spectrum (14) should be studied in this connection, especially as affected by the mode of stimulation (X-rays, cathode rays, heating or monochromatic light of different wave-lengths). The temperature, electric or magnetic field could be changed about the phosphorescing body. The effect of change of state (15) should be tried if this is possible, also any possible changes of valency of the atoms (16) composing the body investigated. We shall attack the problem from all of these standpoints.

After correlating the data obtained by the above named investigations it is pretty certain that it will be possible to take each vibrator and trace the effects produced upon it by the above changes. It is also quite certain that we shall also know something of the nature of the vibrating system and the part that it plays in that complex body we call the atom. We shall now describe a few results obtained by changing the concentration and temperature of a solution of the chemical compound whose absorption spectrum we are studying.

#### IX. THE EFFECT OF RISE IN TEMPERATURE ON THE ABSORPTION SPECTRUM OF CERTAIN SALTS IN AQUEOUS SOLUTION.

##### (a) *Uranous Chloride (B, Plate VII.).*

To a normal solution of uranyl chloride in water was added a small amount of hydrochloric acid and zinc. The production of hydrogen reduced the uranyl to the uranous state. The same can be done in some cases by simply passing hydrogen gas through the uranyl solution. The solution was placed in the glass trough and a temperature run made as in the usual manner. The thickness of layer was 1 mm. The length of exposure was 50 sec. to the Nernst glower and 4 mins. to the spark, the current through the glower being 0.8 amperes and the slit width 0.20 mm. Starting with the strip nearest the comparison scale the temperatures were 8°, 17°, 33°, 48°, 62° and 73°. An exposure was also made at 80° which is not shown in the spectrogram *B*.

At 8° a mist formed on the prisms and for this reason the spectrum film taken at this temperature is much underexposed and the bands appear wider than at the higher temperatures. At this tem-

perature there is complete absorption of the shorter wave-lengths to  $\lambda$  3650. A blue-violet absorption extends between  $\lambda$  4050 and  $\lambda$  4450. Following this band are three strong bands of about equal intensity and each almost 100 Ångström units wide. Their wave-lengths are approximately  $\lambda$  4590, 4760 and 4970. Following is a band at  $\lambda$  5500, a wide band from  $\lambda$  6400 to  $\lambda$  6630 and a rather narrow band at  $\lambda$  6740.

The absorption does not change very greatly until a temperature of  $60^\circ$  is reached. Above this temperature the increase in absorption is quite rapid as the temperature rises. At  $73^\circ$  the ultra-violet band has widened to  $\lambda$  3800, the blue-violet band covers the region from  $\lambda$  4050 to  $\lambda$  5000. The bands  $\lambda$  4600, 4770 and 4980 at  $8^\circ$  have shifted slightly to the red with rise of temperature.

None of the other bands seem to shift to the red at all and the broadening seems to be quite symmetrical. The band at  $\lambda$  5500 has become about twice as wide as it was at the lower temperatures and the two red bands have merged into one band running from  $\lambda$  6350 to  $\lambda$  6800. Between  $73^\circ$  and  $80^\circ$  the absorption increases very greatly. All short wave-lengths are absorbed up to  $\lambda$  5050. The band in the green runs from  $\lambda$  5450 to  $\lambda$  5600 and the band in the red has also widened very greatly, extending from  $\lambda$  6200 to  $\lambda$  6800.

(b) *Copper Bromide (A and B, Plate VIII.)*.

The two spectrograms showing the absorption spectra of copper bromide in water for various temperatures were made for different concentrations of the salt. *A* gives the absorption of a 2.06 normal solution 1 mm. thick and *B* the absorption of a 0.25 normal solution 8 mm. thick. The time of exposure to the Nernst glower was 2 mins. (current 0.8 amperes and slit width 0.20 mm.) and to the spark 6 mins. Starting with the strip nearest the comparison scale the temperatures at which exposures were made for *A* were  $6^\circ$ ,  $17^\circ$ ,  $30^\circ$ , and  $45^\circ$ ; for *B*  $6^\circ$ ,  $17^\circ$ ,  $31^\circ$ ,  $46^\circ$ ,  $59^\circ$ ,  $71^\circ$ , and  $85^\circ$ .

As the spectrograms show, the effect of change of temperature on the absorption spectrum is very marked. Above  $45^\circ$  the concentrated solution did not transmit enough light to affect the photographic film.

(c) *Chromium, Calcium and Aluminium Chlorides (A and B, Plate IX.).*

*A*, Plate IX., represents a spectrogram showing the effect of rise of temperature on an aqueous solution of chromium and aluminium chlorides. The concentration of the chromium chloride was 0.125 normal, and of the aluminium chloride 2.28 normal. The depth of layer was 9 mm. The length of exposure to the Nernst glower was 4 mins. (current 0.8 amperes and slit width .20 mm.) and to the spark 6 mins. Starting with the strip adjacent to the comparison scale the temperatures were 6°, 19°, 36°, 51°, 66° and 81°.

The most marked effect of the aluminium chloride was the production of a very pronounced unsymmetrical broadening, which does not occur when a pure aqueous solution of chromium chloride is heated. At 6° the ultra-violet band extends to  $\lambda$ 3000, at 81° to  $\lambda$ 3300, a much greater widening than takes place for a chromium chloride solution in water. At 6° the blue-violet band extends from  $\lambda$ 4100 to  $\lambda$ 4600 and the yellow band from  $\lambda$ 5800 to  $\lambda$ 6200. Not only do the red sides of the blue-violet and yellow bands widen out enormously towards the red, but the short wave-length edges of these bands actually move towards the red. This effect is much more pronounced in the changes of temperature from 51° to 66° and from 66° to 81°. At 81° the blue-violet band extends from  $\lambda$ 4150 to  $\lambda$ 5050 and the yellow band from  $\lambda$ 5900 throughout the remaining portion of the spectrum, as far as the film is sensitive. The fine chromium bands in the red do not appear.

*B*, Plate IX., is a spectrogram, giving the absorption spectrum of a .125 normal concentration of chromium chloride and a 3.45 normal concentration of calcium chloride in water at different temperatures. The length of the solution was 9 mm., the length of the exposures to the Nernst glower were for 5 min. and to the spark for 6 min. The current through the glower was 0.8 amperes and the slit width 0.20 mm. Starting with the strip adjacent to the comparison scale the temperatures at which the exposures were made were 6°, 19°, 31°, 45°, 64° and 80°.

The effect of rise of temperature upon the absorption spectrum of a mixture of chromium chloride and calcium chloride is very similar to the effect on the mixture of chromium chloride and

aluminium chloride. The blue-violet and the yellow bands widen unsymmetrically and the short wave-length edges of these bands apparently moves towards the red at the higher temperatures.

At 6° the ultra-violet band extends to  $\lambda 2800$ , the blue-violet band from  $\lambda 4000$  to  $\lambda 4400$  and the yellow band from  $\lambda 5600$  to  $\lambda 6100$ . At 64° the ultra-violet band extends to  $\lambda 3100$ , the blue-violet band from  $\lambda 4000$  to  $\lambda 4600$  and the yellow band from  $\lambda 5650$  to  $\lambda 6300$ . At 80° the ultra-violet band extends to  $\lambda 3250$ , the blue-violet band from  $\lambda 3950$  to  $\lambda 5000$  and the yellow band from  $\lambda 5700$  throughout the red end of the spectrum as far as the film is sensitive.

(d) *Uranyl Chloride (A and B, Plate X.)*

A spectrogram (*A*, Plate X.) was made of the absorption spectrum of a normal aqueous solution of uranyl chloride, the depth of cell being 3 mm. Exposures were made to the Nernst glowler for 90 sec., current 0.8 amperes and slit width 0.20 mm. The time of exposure to the spark was 6 min. Starting from the comparison spectrum the temperatures were 6°, 18°, 34°, 52°, 68° and 82°.

At 8° the ultra-violet band extended to  $\lambda 3550$ , the blue-violet band from  $\lambda 4000$  to  $\lambda 4450$ . The bands *a*, *b* and *c* appeared, but the *a* band is very faint. The wave-lengths of the *b* and *c* bands were  $\lambda \lambda 4565$  and  $4725$ .

At 82° the ultra-violet band extends to  $\lambda 3700$ , and the blue-violet band from  $\lambda 3950$  to  $\lambda 4600$ . At this temperature only the *b* band appears,—*a* being very weak and *c* being completely merged into the blue-violet absorption band. The *b* band is located at  $\lambda 4755$ .

A spectrogram, *B*, Plate X., was made of a uranyl chloride water solution 0.0156 normal concentration and a depth of layer of 196 mm. Exposures were made to the Nernst glowler for 30 sec., current 0.8 amperes and slit width 0.20 mm. No exposures were made to the spark except for comparison spectra. Starting with the numbered scale the temperatures were 6°, 18°, 29°, 44°, 59°, 71° and 79°.

For this concentration there is a very slight temperature effect. There is a very faint transmission band between the ultra-violet and blue-violet bands. This is extremely faint and is practically un-

affected by temperature. The blue-violet band widened slightly with rise in temperature. The uranyl bands in the concentrated solution were much stronger and wider than in the dilute solution.

(c) *Neodymium Salts.*

A spectrogram (*A*, Plate XI.) of the absorption spectrum as affected by change of temperature was made of neodymium chloride solution in water, the concentration being 3.4 normal and the depth of layer 12 mm. The length of exposure was 2 min. to the Nernst glower, current 0.8 amperes; slit width .20 mm. The time of exposure to the spark was 6 min. Starting with the strip nearest the numbered scale the temperatures were 11°, 22°, 33°, 45°, 59°, 73° and 85°.

An absorption band appears at about  $\lambda$  2970 for the 11° temperature, a very strong band from  $\lambda$  3250 to  $\lambda$  3285 and an adjacent band from  $\lambda$  3285 to  $\lambda$  3310. At 11° a very narrow and feeble transmission band separates these two bands. At 85° the transmission band has weakened very much. At 11° a very strong band lies between  $\lambda$  3490 and  $\lambda$  3580. The band  $\lambda$  4274 is about 8 Ångström units wide. An extremely narrow band appears at  $\lambda$  4297,  $\lambda$  4306 and  $\lambda$  4324. At  $\lambda$  4234 is a wider and rather diffuse band, it being about 12 Ångström units wide. Bands at 11° lie between  $\lambda$  4415 and 4470,  $\lambda$  4580 and 4650,  $\lambda$  4665 and 4710,  $\lambda$  4740 and 4775,  $\lambda$  4815 and 4835, and the very wide bands  $\lambda$  5010 and 5300 and  $\lambda$  5665 and 5935. Weak bands are located at  $\lambda$  4645,  $\lambda$  4800,  $\lambda$  5320,  $\lambda$  6235,  $\lambda$  6255,  $\lambda$  6280,  $\lambda$  6305 and  $\lambda$  6380. Rather diffuse bands appear at  $\lambda$  6780 and 6840, at  $\lambda$  6850 and from  $\lambda$  6870 to  $\lambda$  6920.

The effect of rise of temperature from 11° to 85° is quite noticeable, although it is not great. In the ultra-violet there is a slight increase in the general absorption. The band  $\lambda$  3285 and 3310 widens slightly. The band  $\lambda$  3490–3580 at 11° has widened so that at 85° it extends from  $\lambda$  3450 to  $\lambda$  3600. The band at  $\lambda$  4415 and 4470 has widened but little. The group of bands from  $\lambda$  4600 to  $\lambda$  4800 have also widened but little. The faint diffuse bands  $\lambda$  4645 and 4800 have practically disappeared. The bands  $\lambda$  5010 and 5300 and  $\lambda$  5665 and 5935 at 11° have widened at 85° to

$\lambda\lambda$  5010 and 5350 and  $\lambda\lambda$  5660 and 5985. The widening of the latter band is distinctly unsymmetrical. The existence of the band  $\lambda$  5320 causes the band  $\lambda$  5010 to  $\lambda$  5300 to widen unsymmetrically.

The bands in the region  $\lambda$  6300 become less sharp as the temperature rises. At  $11^\circ$  there was considerable transmission in the region  $\lambda$  6850. At  $85^\circ$ , however, this transmission disappears and there is practically complete absorption from  $\lambda$  6760 to  $\lambda$  6920. The very sharp bands  $\lambda\lambda$  4282, 4300, 4310, 4322 and 4343 do not appear to change very much with change in temperature. On the strip taken at  $73^\circ$  these bands appear sharper than on any of the other strips.

A spectrogram (*B*, Plate XI.) showing the effect of rise in temperature was made on a neodymium chloride solution in water of c.17 normal concentration and a depth of layer of 196 mm. The amount of neodymium chloride in the path of the light is approximately the same as in the spectrogram, showing the effect of temperature upon a 3.4 normal concentration and a depth of cell of 12 mm. In this case the temperatures were  $5^\circ$ ,  $16^\circ$ ,  $28^\circ$ ,  $42^\circ$ ,  $59^\circ$ ,  $72^\circ$  and  $82^\circ$ . Exposures were made to the Nernst glower for 3 mm. current 0.8 amperes and slit width 0.20 mm. Each strip was exposed to the spark for 6 mm. The purpose of making this spectrogram was to find the effect of concentration of a salt upon the changes produced by change in temperature.

A description of the bands at  $5^\circ$  and  $82^\circ$  will be given. Any change between these two temperatures that takes place is a gradual one. Transmission begins at  $\lambda$  2600. Bands appear between  $\lambda\lambda$  3250 and 3300 and  $\lambda\lambda$  3455 and 3575. The band  $\lambda$  4274 is much sharper and narrower than for the more concentrated solution. The numerous fine bands in the region  $\lambda$  4300 are very faint. The bands  $\lambda\lambda$  4420 to 4460,  $\lambda\lambda$  4600 to 4630,  $\lambda$  4645,  $\lambda\lambda$  4680 to 4705,  $\lambda\lambda$  4745 to 4770 and  $\lambda$  4820 have rather diffuse edges. Wide bands appear from  $\lambda$  5020 to  $\lambda$  5290 and from  $\lambda$  5685 to  $\lambda$  5920. Diffuse bands are located at  $\lambda$  5310,  $\lambda$  6810 and  $\lambda$  6900. The group in the region  $\lambda$  6300 appear, but they are extremely faint.

At  $82^\circ$  the general absorption has increased in the ultra-violet and has reached to about  $\lambda$  2800. It will be noticed here that the effect of rise in temperature is greater upon this general ultra-violet



absorption in the dilute solution, than it is for the concentrated solution previously described.

The band  $\lambda\lambda$  3455 to 3575 at  $5^\circ$  has widened slightly, having the limits  $\lambda\lambda$  3445 and 3580 at  $82^\circ$ , the widening being about 15 Ångström units. This band in the concentrated solution widened 60 Ångström units. Practically no effect of temperature is to be noticed upon the bands from  $\lambda$  4200 to  $\lambda$  4900 with rise in temperature. At the higher temperatures the bands are slightly more diffuse, but this change is very small. The band  $\lambda\lambda$  5020 to 5290 at  $5^\circ$  has widened to  $\lambda\lambda$  5015 and 5285, about 10 Ångström units. The corresponding widening for the concentrated solution was approximately 50 Ångström units, although it must be noted that in the more concentrated solution this widening was mostly due to the increased absorption of the band  $\lambda$  5310 at the higher temperatures. The band  $\lambda$  5685 to  $\lambda$  5920 at  $5^\circ$  has widened to  $\lambda\lambda$  5775 and 5930, about 20 Ångström units, compared with a widening of 55 Ångström units for the more concentrated solutions. None of the other bands show any appreciable change with change in temperature.

A spectrogram (*A*, Plate XII.) was made showing the effect of temperature upon the absorption spectrum of a 1.66 normal aqueous solution of neodymium bromide, the depth of layer being 6 mm. An exposure of 4 mm. was made to the Nernst glower, at .8 amperes and a slit width of 0.20 mm. The length of exposure to the spark was 6 mins. The temperatures of exposure, starting with the strip adjacent to the comparison spark, were  $4^\circ$ ,  $20^\circ$ ,  $36^\circ$ ,  $50^\circ$ ,  $68^\circ$  and  $83^\circ$ .

At  $4^\circ$  there is complete absorption in the ultra-violet up to  $\lambda$  2600. A broad absorption band appears at  $\lambda$  2660 to  $\lambda$  2800 and from  $\lambda$  2950 to  $\lambda$  3060. These absorption bands appear with a more or less general absorption. Bands appear at  $\lambda\lambda$  3460, 3500 and 3540. The band at 4274 is weak. Weak and diffuse bands occur at  $\lambda\lambda$  4440, 4630, 4695, 4760, 4825, 5095, 5260, 6810 and 6900. Wider bands are located at  $\lambda\lambda$  5116 to 5140,  $\lambda\lambda$  5200 to 5240 and  $\lambda\lambda$  5710 to 5850.

At  $83^\circ$  the spectrum is almost exactly the same as at  $4^\circ$ . The ultra-violet absorption is complete up to  $\lambda$  3050. The bands at  $\lambda$  3500 have increased in width slightly and the band  $\lambda$  4274 is

slightly broader. The bands that have widened appreciably are  $\lambda\lambda$  5195 to 5260 and  $\lambda\lambda$  5700 to 5880. The change in the absorption is greatest when the temperature is changed from 68° to 83°. Up to 68° there is practically no change in the absorption spectrum at all.

A spectrogram (*B*, Plate XII.) showing the effect of temperature was made, using an aqueous solution of .055 normal concentration of neodymium bromide, the depth of the layer being 197.4 mm. This spectrogram was made to compare with that taken with a 1.66 normal concentration of the same salt and a depth of layer of 6 mm. The exposures to the Nernst glower lasted 90 sec. in this case, current 0.8 amperes and slit width of 0.20 mm. The length of exposure to the spark was 6 mins. Starting with the strip nearest to the comparison scale the temperatures of the solution were 5°, 16°, 29°, 42°, 55°, 68° and 84°.

At 5° there is practically complete transmission of light between  $\lambda$  3400 and  $\lambda$  2600, no ultra-violet bands appearing, as was the case for the more concentrated solution. The bands  $\lambda\lambda$  4445, 4693, 4760, 4825 and 5095 were somewhat sharper than they were in the concentrated solutions. The two largest bands extended from  $\lambda$  5200 to  $\lambda$  5250 and from  $\lambda$  5710 to 5850. As in the case of the more concentrated solution, so here, the greatest change in the absorption took place in the change from 68° to 84°. The ultra-violet absorption increased up to  $\lambda$  2900. The bands at  $\lambda$  3500 became considerably stronger, but they widened very little. The bands  $\lambda\lambda$  4445, 4693, 4760 and 4825 are somewhat weaker than at 5°. The wide bands remained practically as wide as at 5°,  $\lambda$  5200 to  $\lambda$  5250 and  $\lambda$  5705 to 5870. This indicates a widening of about 25 Ångström units for the latter band. For the more concentrated solution the widening of these two bands was 25 and 40 Ångström units respectively. It is thus seen that in the more concentrated solutions the bands widen more with rise in temperature than they do in the less concentrated solutions. At 42° in the dilute solution there appears a narrow band at  $\lambda$  6710. This increases in intensity with rise in temperature. This band does not appear at all in the concentrated solution.

A spectrogram (*A*, Plate XIII.) was made of neodymium chloride and calcium chloride in water. Exposures were made for 30 sec.

to the Nernst glower, the current being 0.8 amperes and the slit width 0.20 mm. The length of exposure to the spark was 4 mins. Starting with the strip nearest the numbered scale the temperatures were 6°, 17°, 31°, 49°, 63°, 74° and 82°.

The general effect of the addition of calcium chloride is to make all the bands hazier, and to increase the transmission throughout the region of the band. At 6° there is a slight transmission throughout the ultra-violet portion of the spectrum. As the temperature is raised this general transmission is decreased, and at 82° practically no light passes through the solution of shorter wave-length than  $\lambda 2800$ . Sharp bands occur at  $\lambda 3464$ ,  $\lambda 3500$ ,  $\lambda 3535$ ,  $\lambda 4276$  and weak diffuse bands at  $\lambda 4295$ ,  $\lambda 4305$ ,  $\lambda 4340$ ,  $\lambda 4445$ ,  $\lambda 4620$ ,  $\lambda 4695$ ,  $\lambda 4760$ ,  $\lambda 4825$ ,  $\lambda 5095$ ,  $\lambda 5130$ ,  $\lambda 5225$ ,  $\lambda 5260$ ,  $\lambda 5320$ ,  $\lambda 5710$ , to  $\lambda 5860$ ,  $\lambda 6245$ ,  $\lambda 6810$  and  $\lambda 6900$ .

At 82° the bands in the  $\lambda 3500$  region are slightly more intense than at 6°. Practically all the bands from  $\lambda 4200$  to  $\lambda 5200$  have become much weaker at the higher temperature. This is especially true of the band  $\lambda 4276$ , its intensity being less than half what it is at 6°. Most of the bands are shifted to the red with reference to the same bands at 6°. For instance,  $\lambda 5095$  is shifted 5 Ångström units towards the red. The bands  $\lambda 4695$ ,  $\lambda 4760$  and  $\lambda 4825$  are all shifted to the red at the higher temperature, and especially  $\lambda 4825$ , the shift in this case amounting to 5 Ångström units. In the case of these bands the shift is not an apparent one due to unsymmetrical broadening, for in this instance there is no broadening at all.

The band from  $\lambda 5710$  to  $\lambda 5860$  at 6° has widened very unsymmetrically and has the limits  $\lambda 5710$  to  $\lambda 5920$ . The short wave-length side is quite sharp and its position is practically independent of the temperature. The long wave-length edge is quite broad and recedes quite rapidly towards the red as the temperature is raised. The bands in the red  $\lambda 6810$  and  $6900$  grow fainter and fainter with rise in temperature, and have practically disappeared at 82°. The band  $\lambda 6245$  is very weak at 6° and has disappeared at about 60°.

It will thus be seen that not only does the presence of calcium chloride modify greatly the absorption of neodymium chloride, but that it changes the effects due to temperature very fundamentally. In pure neodymium chloride practically no bands decrease in in-

tensity with rise in temperature, and at present no shift has been detected. When calcium chloride is added to the solution most of the bands decrease in intensity with rise in temperature and several are shifted towards the red at the same time. Several bands disappear. Moreover, the band  $\lambda\lambda 6800$  to  $6900$ , although it widens, this widening is entirely on the red side, whereas for the pure neodymium chloride solution this widening always takes place on both sides of the band.

A spectrogram (*B*, Plate XIII.) was made to show the effect of change in temperature upon a 2.15 normal aqueous solution of neodymium nitrate. The length of layer was 3 mm. The exposures were for 40 sec. to the Nernst glower, current 0.8 amperes, slit width .20 mm. The length of exposure to the spark was 6 mins. Starting with the strip nearest the comparison spark the temperatures were  $4^\circ$ ,  $17^\circ$ ,  $29^\circ$ ,  $43^\circ$ ,  $58^\circ$ ,  $71^\circ$  and  $84^\circ$ .

The changes in the spectrum due to this change in temperature of  $80^\circ$  was very slight. The  $\text{NO}_3$  band extends to about  $\lambda 3250$  at  $4^\circ$ , and to about  $\lambda 3280$  at  $84^\circ$ . The bands at  $\lambda 3500$  became considerably wider and their edges more diffuse at the higher temperatures. At the lower temperatures fine bands appear at  $\lambda\lambda 5210$ ,  $5225$  and  $5240$ . At  $84^\circ$  these bands all merge into a single band. The red band extends from  $\lambda 5705$  to  $5860$  at  $4^\circ$ . The band at  $\lambda 5820$  is very faint at the lower temperatures. At  $84^\circ$  it is unrecognizable. At this temperature the red band extends from  $\lambda 5700$  to  $\lambda 5880$ . The widening of this band for the concentrated solution is somewhat greater than for the dilute solution, but the effect of concentration is very slight. This is to be expected since the effect of temperature itself is so very minute.

A spectrogram (*A*, Plate XIV.) was made of an aqueous solution of neodymium bromide 1.66 normal concentration and 54.6 mm. depth of cell. The exposures were 3 mins. to the Nernst glower and 6 mins. to the spark. The current in the Nernst glower was 0.8 amperes and the slit width 0.20 mm. Starting with the strip nearest the comparison scale the temperatures were  $6^\circ$ ,  $20^\circ$ ,  $33^\circ$ ,  $47^\circ$ ,  $62^\circ$ ,  $73^\circ$  and  $82^\circ$ .

The effect of rise in temperature upon the absorption spectra of this salt was quite marked; practically all of the bands broaden-

ing and becoming more intense. At  $6^\circ$  the ultra-violet absorption extended to  $\lambda 3600$ . At  $82^\circ$  it had advanced to  $\lambda 3800$ . Very narrow and fine bands appear at  $\lambda 4186$ ,  $\lambda 4300$ ,  $\lambda 4308$ ,  $4345$ ,  $6240$ ,  $6265$ ,  $6290$ ,  $6305$ , and much broader bands at  $\lambda 6380$  and  $\lambda 6740$ . Wide bands occur at from  $\lambda 4390$  to  $4480$ ,  $\lambda 4550$  to  $4850$ ,  $\lambda 4990$  to  $5340$ ,  $\lambda 5650$  to  $5950$  and  $\lambda 6760$  to  $6930$ , at  $6^\circ$ . At  $82^\circ$  these bands have the following limits respectively:  $\lambda 4380$  to  $4500$ ,  $\lambda 4540$  to  $4910$ ,  $\lambda 4960$  to  $5370$ ,  $\lambda 5620$  to  $5990$  and  $\lambda 6730$  to  $6960$ .

(f) *Erbium Chloride.*

A spectrogram (*B*, Plate XIV.) was made to show the effect of rise in temperature upon the absorption spectrum of a solution of erbium chloride. For this purpose a 0.94 normal solution of erbium was used and the depth of layer was 48 mm. The solution probably contained a considerable number of impurities, so that in fact the amount of erbium was quite small. The absorption spectrum was found to change but little with rise in temperature, thus indicating a dilute solution. Exposures were made for 30 sec. to the Nernst glower and 4 mins. to the spark. The current through the glower was 0.8 amperes and the slit width 0.20 mm. Starting with the spectrum nearest the comparison scale the temperatures were  $7^\circ$ ,  $17^\circ$ ,  $29^\circ$ ,  $46^\circ$ ,  $60^\circ$ ,  $70^\circ$  and  $80^\circ$ .

At  $70^\circ$  the ultra-violet is absorbed to  $\lambda 3950$ . As the temperature is raised the ultra-violet absorption increases, and at  $80^\circ$  it reaches  $\lambda 3150$ . Bands from 20 to 40 Ångström units wide occur at  $\lambda 3235$ ,  $\lambda 3510$ ,  $\lambda 3640$  and  $\lambda 3785$ . These bands are slightly wider at  $80^\circ$ , but as for all the other erbium bands this widening is very small. Weak and narrow bands appear at  $\lambda 4165$ ,  $4425$ ,  $4458$ ,  $4500$  (strong),  $4535$ ,  $4540$ ,  $4555$ ,  $4580$ ,  $4685$ ,  $4750$  (30 Å. u. wide),  $4810$ ,  $4840$ ,  $4855$ ,  $4870$  (strong and 20 Å. u. wide), and  $4920$ ,  $\lambda 4920$  lies alongside of a fuzzy band extending from  $\lambda 4910$  to  $\lambda 4950$ .

After these comes a rather wide band which for a shorter length of layer would most likely be broken up into a number of much finer bands. This band extends from  $\lambda 5190$  to  $\lambda 5250$ . At  $\lambda 5217$  there runs a narrow sharp line through the fuzzier and wider band. Broad (about 30 Å. u. wide) and very faint bands are located at  $\lambda 5630$  and  $\lambda 5760$ . For greater concentrations these would prob-

ably show as finer bands. The band at  $\lambda 6540$  is much more diffuse on the red than on the violet side; this possibly being due to a component that is not separated at this temperature. Other bands are located at  $\lambda\lambda 5365, 5380, 5425, 5445, 5505, 6410, 6440, 6495$  and  $6690$ .

The general effect of rise in temperature here is to cause the lines to become slightly fuzzier and to show more of a "washed out" appearance. No shift due to rise in temperature was noticed.

Throughout all the previous work the wave-lengths were read directly from a scale. This scale was made so as to give the wave-lengths in Ångström units directly. It was found in the measurements that the Seed films did not correspond to the Wratten and Wainwright films, when the same spark spectra on the two kinds of films were placed beside one another. This was probably due to different shrinkage of the two kinds of films on fixing, washing and drying. For this reason the wave-length measurements are not intended to be absolutely correct but only relatively so. All the temperature work was done with Wratten and Wainwright films. The relative measurements of fine bands for any spectrogram are probably correct to within a few Ångström units.

#### X. SUMMARY.

The absorption spectra of the uranyl salts contain a series of bands in the blue and violet. Twelve of these bands can usually be detected for each salt. Starting from the blue end of the series the bands are designated by the letters *a, b, c*, etc. These bands are usually diffuse and from 30 to 50 Ångström units wide.

The uranyl bands of uranyl nitrate in water are all farther to the violet than the uranyl bands of any other salt investigated, or of uranyl nitrate in other solvents.

The uranyl absorption bands of crystals of uranyl nitrate agree with the absorption bands of an aqueous solution of the nitrate, with the exception of the *f, g, h* and *i* bands; these latter being shifted to the red in the crystal.

Dilution within the ranges studied does not affect the position of the uranyl bands. Theoretically, all the uranyl salts in water

should give the bands of the same wave-lengths for very dilute solutions.

The uranyl bands of the nitrate in methyl alcohol are all shifted to the red about 50 Ångström units, with reference to the bands in water. Mixtures of water and methyl alcohol show that we have both sets of bands existing for the same solution, the "water" bands increasing in intensity as the amount of water increases. The water bands are the more persistent. This indicates the existence of a hydrate and an alcoholate of the uranyl group. In ethyl alcohol the *a*, *b*, *c* and *d* bands are shifted to the red with reference to the methyl alcohol bands. The other bands appear to have the same positions as the methyl alcohol bands.

The absorption spectrum of the anhydrous salt is very complex and the bands could not be recognized.

The bands of uranyl bromide in water, of uranyl acetate in water and methyl alcohol, and also of the anhydrous salt, are approximately of the same wave-lengths, differing but slightly from the wave-lengths of the uranyl nitrate bands of an aqueous solution.

The bands of uranyl sulphate in water are all shifted towards the red about 50 Ångström units, with reference to the uranyl nitrate bands in water. For both the sulphate and nitrate in water the bands are very much alike. The *i* band is very weak in both cases.

Uranyl chloride bands of an aqueous solution are shifted to the red with reference to the uranyl nitrate bands of an alcoholic solution. The addition of calcium chloride or aluminium chloride is found to produce very marked effects upon the uranyl chloride bands. The addition of sufficient aluminium chloride to a water solution of uranyl chloride, or of calcium chloride to a methyl alcohol solution of uranyl chloride is found to cause the *d* and *e* bands to come together, so as to form a single wide band, and to cause the other uranyl bands to shift so that the whole resulting series of bands is almost identical with the series of bands of an ethyl alcohol solution of uranyl chloride. The effect of adding foreign substances also greatly modifies the intensity of the bands. An example of this difference of action is the effect of adding aluminium chloride to an aqueous solution of uranyl chloride. The

*a* and *b* bands are affected entirely differently; the *a* band being very much reduced in intensity and made narrower, whereas the *b* band becomes very much stronger and wider.

A new set of fine bands in the green has been discovered in the absorption spectrum of an aqueous solution of uranyl chloride. These only appear for pure water solutions; a small amount of aluminium or calcium chloride causing them to vanish. They do not appear for methyl or ethyl alcohol solutions, and for no other uranyl salt except very faintly for the sulphate.

The absorption spectrum of several uranous salts has been photographed. The spectrum is entirely different from that of the uranyl compounds. The absorption spectra of uranous chloride in methyl alcohol and in water were found to be very different. The absorption spectrum of neodymium chloride in glycerol was found to be entirely different from that of the salt in water. Mixtures of water and glycerol seem to indicate the existence of both sets of bands in the same solution. The "glycerol" bands are more persistent with reference to water bands than "alcohol" bands are. Much more work along this line is contemplated.

Rise in temperature has been found in general to cause an increase in the amount of absorption, and to cause the absorption bands to widen. This widening of the bands may or may not be symmetrical.

Some of the absorption bands of uranous chloride widen very rapidly with rise in temperature. Other bands do not widen so rapidly, and seem to be slightly shifted towards the red.

In solutions containing a single salt, it has invariably been found that the bands widen with rise in temperature, and that this widening is greater, the greater the concentration of the solution.

The uranyl bands of aqueous solutions of the chloride and sulphate of uranyl are shifted towards the red with rise in temperature. The intensity of the uranyl bands does not seem greatly modified by changes in temperature.

The effect of rise in temperature on the absorption spectrum of a solution of a salt containing calcium or aluminium chloride is very peculiar. The bands usually broaden very unsymmetrically,



and in all cases investigated, the widening has been on the longer wave-length edge. A typical example is shown in Plate III.

Rise in temperature causes the neodymium bands to widen slightly, but no shift of the bands has been noticed. However, when calcium chloride has been added to the neodymium solution, a rise of temperature causes many of the bands to become much less intense, and also causes some of the bands to shift to the red. In the recent work of Becquerel and others it is quite possible that the presence of various foreign bodies in the crystals along with the neodymium may have a very great influence upon the absorption spectrum.

All the above conclusions must be understood to be limited to the conditions and within the ranges described in the earlier parts of this paper.

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